Report 155

April, 1957

THE GYPSUM REQUIREMENT OF ALKALI SOILS

Agricultural Experiment Station

The University of Arizona

Tucson, Arizona

Report 155

April, 1957

THE GYPSUM REQUIREMENT OF ALKALI SOILS

Agricultural Experiment Station

The University of Arizona

Tucson, Arizona

THE GYPSUM REQUIREMENT OF

ALKALI SOILS

W. T. McGeorge

This manuscript is a report of research on the study of quantitative methods for determining the gypsum requirement of alkali soils. It represents a part of the research being conducted under Western Regional Project W-30 "Measurement, Evaluation, and Modification of Soil Structure" and was supported in part by regional funds.

TABLES

FIGURES

TABLE OF CONTENTS

THE GYPSUM REQUIREMENT OF ALKALI SOILS

By W. T. McGeorge[1]

Department of Agricultural Chemistry & Soils

University of Arizona Agricultural Experiment Station

INTRODUCTION

An important phase of saline and alkali soil research is that concerned with the development of chemical and physical tests that may be useful in their appraisal. Some of the factors which influence the chemical and physical properties of these soils and the growth of plants thereon are: total soluble salt concentration in the soil solution, soluble and exchangeable sodium, pH value, ratio of Na to Ca in the soil solution, and texture. Saline and alkali soils have been conveniently classified in the Agricultural Handbook No. 60 edited by the staff of the U. S. Salinity Laboratory (10).

For a salinity test, the conductivity of the saturation extract is quite satisfactory and is widely used for appraising the salinity status of a soil. For the alkalinity test, the pH determination is simple and rapid but has limited application to the apprisal of alkali soils except in the case of soils which are very high in the pH range. The pH of the soil is influenced by a number of factors, particularly by the soil-water ratio used for the determination and salt content of the soil. Because of these factors, the pH value does not always give a true picture of the alkali or exchangeable sodium status of the soil.

With the exception of the so-called potassium and magnesium alkali soils, which are found less frequently than sodium alkali soils, the presence of alkalinity is largely determined by the sodium percentage in the exchange complex or the ratio between sodium and calcium in the exchange complex and the soil solution. The determination of exchangeable sodium in the soil is a time-consuming procedure and such an analysis, for the appraisal of an alkali soil, if oftentimes not feasible.

One of the major problems in irrigation agriculture in the Southwest is that of replacement of calcium (Ca) ions in the clay fraction of the soil by sodium (Na) ions. This may occur because of a high Na to Ca ratio in the irrigation water or in the soil solution. When the exchangeable sodium in the clay fraction reaches a certain percentage, the accompanying changes in physical and chemical properties of the soil seriously restrict plant growth and crop production. There is a considerable difference in the binding force between calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na); the latter being least firmly held. Therefore, adsorbed sodium may be readily replaced in the soil by calcium ions applied as a corrective. If the soil is a type that can be easily drained, the sodium replacement does not impose a serious problem. Clay soils have a high exchange capacity and a high percentage of particle sizes which are dispersible; therefore, if the soil has a high clay percentage or possesses other properties which make drainage difficult, sodium replacement by calcium becomes a real problem. The replacement of sodium ions by calcium ions in the soil is a contact reaction and, therefore, when soluble calcium salts are added to the soil, the free movement of calcium ions throughout the

---

[1]Agricultural Chemist Emeritus, retired June 30, 1956.

soil is essential for reclamation. A breakdown in structure is far more serious in a clay than a sandy soil because of the inherently slow rate of water penetration and drainage.

The fundamental theories on which the reclamation of alkali soil is based are well known. Primarily, the soil treatment involves the use of a soil corrective, sometimes referred to as a conditioner or amendment, which is either a direct or an indirect source of soluble calcium. Gypsum has been used for many years as a soil corrective for the reclamation of alkali soils, and the tonnage still used is greatly in excess of all other correctives. As a mineral there is a plentiful supply of gypsum in the Southwest and the price during practically all of 75 years has been relatively low. For this reason, little attention has been given to the per-acre rate of application. With an increase in the price of gypsum, an awareness of cost and need for its application on a quantitative basis has arisen. If we assume that a soil should not contain in excess of 10 per cent exchangeable sodium in the exchange complex, it is obvious that the quantity of gypsum required to reclaim a soil containing 50 per cent sodium in the exchange complex is far greater than needed for reclaiming a soil with 25 per cent sodium, and the quantity will also depend on the exchange capacity of the soil.

In other words the application of gypsum on a quantitative basis requires a knowledge of the exchange capacity of the soil and the percentage of sodium in the exchange complex. From a recognition of this, and the fact that the determination of exchange capacity and exchangeable sodium is a time-consuming operation, several simple and rapid methods have been developed for determining the gypsum requirement of a soil. A quantitative method for determining the lime requirement of an acid soil has been in profitable use for many years.

A simple and rapid test for appraising the alkalinity of the soil, based on the exchangeable sodium content, should be extremely useful. Since gypsum is the calcium salt most used for sodium replacement, and is widely employed in the reclamation of alkali soils, a gypsum requirement test has been suggested (4).

Gypsum--Gypsum has been used as a conditioner or corrective for alkali soils since about 1890, when it was introduced in California by Hilgard. For many years after gypsum came into general use in the West, sodium carbonate was recognized as the principal alkali salt in black alkali soils. At first, gypsum was recommended only for black alkali soils and not for white alkali soil reclamation. The reaction between gypsum and sodium carbonate is represented by the equation:

$$CaSO_4 \cdot 2H_2O + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4 + 2H_2O$$

This is a reversible reaction and can proceed only to equilibrium unless the sodium sulfate is leached from the soil. It is, therefore, essential that the soil be leached during the process of reclamation.

Adsorbed sodium in the clay minerals, the exchange complex, is presently recognized as the principal source of alkalinity in soils. The reclamation of this type of alkalinity also requires a soluble calcium salt that is relatively cheap. Gypsum, therefore, continues to be the principal soil corrective that meets the requirements for the reclamation of alkali soils. In this case, the reaction is one of replacement, in which the calcium ion replaces the sodium ion in the exchange complex. Soluble sodium salts in the soil solution may interfere or completely interrupt this replacement reaction. The replaced sodium ions become a part of the soil solution when the soil is treated with gypsum, increase the ratio of Na to Ca in the soil solution, and may become sufficiently concentrated in the soil solution to halt reclamation. So, here again, it is necessary to remove the excess of sodium salts, the product of the replacement reaction, from the soil by leaching during the process of reclamation.

There have been many cases where gypsum has failed to alleviate the undesirable soil conditions which are usually associated with the presence of sodium salts in the soil or a high percentage of exchangeable sodium in the exchange complex. Hilgard and Loughridge (4) noted such failures as early as 1895. At that time, Loughridge offered three explanations: 1, gypsum is of value only for black alkali soils; 2, the gypsum may be of poor quality; 3, not enough gypsum was applied (should be 1/3 more than the weight of sodium carbonate in the soil).

During all the years that gypsum and other soil correctives have been used for the reclamation of alkali soils, the application has rarely been made on a quantitative basis; that is, on the basis of the actual gypsum requirement of the soil or the gypsum-absorbing capacity of the soil. Presently, there is increasing awareness of this and also there is increasing evidence that failure of gypsum to alleviate alkali soil conditions is, in many cases, brought about because it has not been added in sufficient quantity.

Objectives--The objectives in the study presented were to review the different methods which have been suggested for determining the gypsum requirement of the soil and to compare the results obtained by the application of a number of these methods to a selected group of soils.

REVIEW OF METHODS

Probably the first semi-quantitative method for determining the gypsum requirement of the soil was that of Loughridge (4) in which he determined the quantity of sodium carbonate in the soil and recommended that gypsum be added at an equivalent rate, plus an excess of one-third over the equivalent rate. In 1945, Gardner (3) proposed mixing a soil sample with varying quantities of gypsum and examining the permeability and capillary rise of water in a vertical column of the treated soil as a means of determining whether the soil will respond to gypsum. In 1947 the U. S. Regional Salinity Laboratory (10) proposed that the gypsum requirement of a soil be calculated from the exchangeable sodium content. In 1951 McGeorge and Breazeale (5) proposed a test for gypsum requirement in which the soil is shaken with gypsum solutions of varying concentrations and the saturation point determined by testing the filtrates for gypsum by mixing the water extract with an equal volume of acetone or alcohol. Schoonover (8) further simplified this method by using a smaller weight of soil and shaking this with a saturated solution of gypsum. A versenate titration of the gypsum solution before and after contact with the soil is the measure of gypsum absorption in this method. Ricardo (7) recommends the following methods: A 100 gram sample of soil is divided into two equal parts "a" and "b". Sample "a" is well mixed with 1 or 2 grams of gypsum, and both portions are separately suspended in 200 ml. of distilled water and filtered. The residues on the filter papers are repeatedly washed with distilled water. The filtrate and washings from "a" will be clear. The filtrate from "b" will be either turbid or relatively clear. If "b" is turbid, the soil cannot be regenerated by simple lixiviation (repeated leaching) and requires treatment with gypsum. If the filtrate and washings from "b" are clear, the soil contains sufficient calcium and is susceptible to renovation by leaching. This method is obviously qualitative, hence, no results are reported in this article. Cottenie (2) and Van Beekom (11) have proposed methods based on the quantity of replaceable sodium in the soil. An ingenious method is that of Shawarbi and Abdel-Bar (9), in which the gypsum requirement of the soil is determined by titrating 10 grams of soil in water suspension with 0.02 normal sulfuric acid.

SOILS USED IN STUDY

Twenty-five soil samples were selected from scattered sections of the State for the study of gypsum requirement methods. They included a wide variety of soils with respect to texture, exchange capacity, and exchangeable Na, K, Mg, and Ca. In gypsum requirement, they range from 0 to 50 tons or more gypsum/acre. Some of the chemical and physical characteristics of these soils are given in Table 1. The exchange capacity varies between 5.5 and 42.7 m.e./100g., the clay percentage between 5 and 62, the exchangeable sodium between 0.2 and 35.2 m.e./100g., sodium percentage between 1.7 and 82.3, exchangeable potassium between 0.1 and 7.4 m.e./100g. and 1.8 and 57.7%, exchangeable magnesium between 1.1 and 8.2 m.e./100g. and 13.6 and 40.0%, and conductivity between 0.8 and 140 mmhos./cm.

Gypsum was present in two of these soils when they were sampled in the field, namely, Nos. 13 and 20. Soil 13 and 12.5% Na in the exchange complex, and soil 14 is this same soil after it had been partially desalinized in the laboratory. This desalinization removed the excess salt and the gypsum present in the soil was sufficient to reduce the sodium percentage to 6.8.

In several of these soils, there was a great excess of soluble salts. In order to determine the effect of salinity on the gypsum requirement test, these highly saline soils were partially desalinized in the laboratory and the gypsum requirement tests made on both the saline and desalinized soils. These soils are identified by the following numbers:

No. 7 represents No. 6 after partial desalinization
No. 14 represents No. 13 after partial desalinization
No. 19 represents No. 18 after partial desalinization

The soils were desalinized by shaking with water, filtering the whole through a Buchner funnel, and washing until water no longer passed readily through the soil.

There are a number of other factors that would be expected to introduce an error in the determination of the gypsum requirement of the soil when the determination is made by shaking the soil with a solution of gypsum. Bicarbonates and carbonates should precipitate some of the soluble calcium added as gypsum. Another source of error is the high sodium percentage in the exchange complex for the soils that are very high in exchangeable sodium. It is not unreasonable to expect that these soils, as well as the saline soils, might require a second treatment with gypsum in order to obtain a near complete replacement of adsorbed sodium.

There is also a question as to whether replaceable potassium and magnesium may introduce an error. Replacement studies in our laboratory (5) indicate that replaceable potassium and magnesium will have little or no influence on replacement of sodium by calcium when the soil is treated with the gypsum solution for the gypsum requirement test. These studies showed that the quantity of potassium and magnesium replaced by a gypsum solution is not significant as long as a moderately high replaceable sodium percentage is present in the soil.

RESULTS

McGeorge-Breazeale Method - The soils were first tested for gypsum requirement by the method developed by McGeorge and Breazeale (5). In this test, a series of 50-gram portions of soil are shaken with 250 mls. of aqueous solutions of gypsum of increasing concentrations as follows: the gypsum concentrations also being expressed as tons per acre (tpa):

50 grams soil	250 mls. distilled water		
50 grams soil	250 mls. distilled water, plus	25 mgms. gypsum	(1 tpa)
50 grams soil	250 mls. distilled water, plus	50 mgms. gypsum	(2 tpa)
50 grams soil	250 mls. distilled water, plus	100 mgms. gypsum	(4 tpa)
50 grams soil	250 mls. distilled water, plus	150 mgms. gypsum	(6 tpa)
50 grams soil	250 mls. distilled water, plus	200 mgms. gypsum	(8 tpa)
50 grams soil	250 mls. distilled water, plus	250 mgms. gypsum	(10 tpa)

Other concentrations of gypsum solution are used if the 10-ton-per-acre application shows a negative test for gypsum in the filtrate. After shaking these soil portions for one hour in the above gypsum solutions, and the one in distilled water for a control, they are filtered. Twenty-five mls. of each filtrate are mixed with 25 mls. of acetone or alcohol. A precipitate shows the presence of gypsum, as gypsum is insoluble in a 1:1 mixture of water and acetone or alcohol. The first in the series that shows the presence of gypsum in the filtrate represents the approximate gypsum requirements of the soil. If the soil is already gypsiferous, the filtrate from the control will give a precipitate when mixed with acetone or alcohol.

The results obtained from this gypsum requirement test on the 25 soil samples are given in Table 2. Only the controls, the treatment which preceded the point where excess of gypsum appeared in the filtrate, and the treatment in which a positive test for gypsum was obtained in the filtrate are given in Table 2 for sake of brevity. The acetone test in a water solution of gypsum is not delicate enough to give a precipitate, in the gypsum requirement test, when gypsum is added to the soil at the rate of 1 ton per acre. This is equivalent to a mixture of 50 grams of soil and 25 mgms. gypsum in 250 mls. of water. If greater accuracy is desired, it is advisable to take this into consideration when interpreting the test.

Schoonover Method - Schoonover (8) has proposed a method by which the gypsum requirement test can be made by a single test rather than a series of tests as in the McGeorge-Breazeale method. His method is as follows: Prepare a saturated solution of gypsum by shaking C. P. gypsum ($CaSO_4$ $2H_2O$) with distilled water. Let settle until clear, or filter. Determine Ca as m.e./liter using versenate titration method. The concentration should be about 30 m.e./ liter. Also, record concentration as ml. standard versenate required to titrate 5 mls. Place 5 gram of the soil to be tested in a flask or bottle. Add exactly 100 mls. of saturated gypsum solution, stopper, and shake at intervals for 10 minutes. Filter through a folder filter. Determine Ca plus Mg in a 5 ml. aliquot. The difference between the Ca plus Mg found in the extract, and the concentration of Ca in the saturated gypsum solution, represents the Ca which would be adsorbed to replace the Na under conditions of a plentiful gypsum supply and excess water. The gypsum requirement per acre-foot or acre-6-inches of soil is calculated from this.

The gypsum requirements of the 25 soil samples as determined by the Schoonover method are given in Table 3 in comparison with the McGeorge-Breazeale method.

Table 1. Some chemical and physical characteristics of soils used in the study of gypsum requirement tests.

Soil No.	Total exchange capacity	Clay	Na in water extract	Exchange-able Na	Exchange-able Na to total exchange capacity	Exchange-able K	Exchange-able K to total exchange capacity	Exchange-able Mg	Exchange-able Mg to total exchange capacity	pH soil paste	pH value in 1 part soil to 10 parts water	Conduc-tivity
	m.e./100g.	%	m.e./100g.	m.e./100g.	%	m.e./100g.	%	m.e./100g.	%			mmhos/cm
1	21.5	31	1.4	1.4	6.5	0.9	4.2	3.4	15.8	8.2	9.5	0.8
2	29.5	44	4.1	4.4	14.9	1.0	3.4	5.8	19.6	8.0	9.7	-
3	34.0	50	3.1	6.4	18.8	1.7	5.0	6.9	20.2	8.3	9.7	4.3
4	5.5	5	0.6	0.6	10.9	0.1	1.8	2.2	40.0	8.1	9.3	1.2
5	22.0	33	1.9	1.5	6.8	0.9	4.1	4.6	20.9	8.2	9.6	1.1
6	16.7	26	35.1	9.5	56.7	2.6	15.1	3.2	19.2	8.3	9.5	55.0
7*	18.4	28	10.2	9.1	49.4	2.7	14.7	2.5	13.6	8.6	10.0	13.0
8	21.1	31	4.8	6.7	31.7	1.8	8.5	4.3	20.4	8.1	9.7	3.5
9	11.3	18	1.0	0.2	1.7	1.9	16.8	4.5	40.0	7.9	8.8	1.9
10	13.5	23	0.8	0.7	5.2	1.1	8.1	3.3	24.4	7.9	8.7	3.0
11	27.3	41	2.5	3.3	12.1	2.1	7.7	5.2	19.0	7.8	8.9	3.0
12	17.0	27	1.3	2.7	15.8	4.6	27.0	3.5	20.7	8.2	9.3	2.6
13	16.0	25	5.4	2.0	12.5	1.3	8.1	6.1	38.1	7.9	8.9	9.0
14*	17.8	27	2.6	1.2	6.8	1.5	8.4	6.1	34.3	7.9	9.0	4.5
15	12.8	20	16.9	4.5	35.0	7.4	57.7	2.0	15.6	8.6	9.6	35.0
16	40.0	60	4.3	7.4	18.5	2.5	6.2	5.9	14.7	7.9	9.1	5.0
17	30.7	52	4.5	7.2	23.4	2.2	7.2	5.4	17.5	7.9	9.4	4.5
18	16.7	26	53.0	7.4	44.3	1.7	10.2	6.3	37.7	7.8	8.6	140.0
19*	17.9	27	7.5	8.9	49.5	1.9	10.6	4.0	22.4	8.5	9.8	9.0
20	21.5	31	14.5	1.2	5.6	7.7	35.8	6.6	30.7	7.4	8.2	47.0
21	30.5	45	4.6	7.2	23.6	2.3	7.5	5.1	16.7	8.2	9.2	6.0
22	42.7	62	11.1	35.2	82.3	3.7	8.7	1.1	25.8	9.8	10.1	21.0
23	12.5	19	7.6	5.2	41.5	1.1	8.8	1.9	15.2	9.9	10.1	6.5
24	28.9	43	1.8	1.6	5.5	1.6	5.5	8.2	28.3	7.8	8.9	1.8
25	12.5	19	-	1.1	8.8	1.3	10.4	4.7	37.5	7.8	8.7	3.4

* Nos. 7, 14, and 19 are the same soils as 6, 13, and 18, but partially desalinized before analysis by leaching with water.

Table 2. Gypsum requirement by McGeorge-Breazeale method, Na in water and gypsum solution extract, Na replaced by Ca in gypsum solution, and conductivity of extract.

Soil No.	Gypsum Requirement Tons/A*	Gypsum Test in Filtrate	Na in Water and Gypsum Sol'n Extract mgms/50g.	Na Replaced by Ca in Gypsum Sol'n** mgms/50g.	Conductivity of Water-Gypsum Sol'n mmhos/cm.
1	0	-	8.3	-	0.2
	4	-	14.3	6.0	0.6
	5	+	15.5	7.2	0.8
2	0	-	39.9	-	0.9
	6	-	61.9	22.0	1.2
	8	+	65.0	25.1	1.4
3	0	-	25.7	-	0.6
	8	-	48.0	22.3	1.2
	10	+	59.4	33.7	1.7
4	0	-	4.8	-	-
	2	-	6.6	1.8	-
	4	+	7.0	2.2	-
5	0	-	13.9	-	0.3
	4	-	22.4	8.5	0.7
	6	+	26.4	12.5	0.9
6	0	-	376.0	-	7.2
	4	-	380.0	4.0	7.4
	6	+	380.0	4.0	7.4
7	0	-	126.0	-	1.9
	12	-	156.0	30.0	3.0
	15	+	160.0	34.0	3.1
8	0	-	40.3	-	0.7
	12	-	71.5	31.2	1.5
	14	+	72.2	31.9	1.7
9	0	-	5.6	-	0.3
	1	-	6.8	1.2	0.4
	2	+	7.5	1.9	0.4
10	0	-	6.0	-	0.3
	1	-	7.4	1.4	0.3
	2	+	7.7	1.7	0.4
11	0	-	24.7	-	0.7
	4	-	30.5	5.8	0.9
	5	+	32.7	8.0	1.1
12	0	-	12.1	-	0.5
	4	-	15.8	3.7	0.8
	6	+	19.3	7.2	1.0
13	0	+	56.9	-	1.5
	2	+	62.0	5.1	1.7

Table 2 - Continued

Soil No.	Gypsum Requirement Tons/A*	Gypsum Test in Filtrate	Na in Water and Gypsum Sol'n Extract mgms/50g.	Na Replaced by Ca in Gypsum Sol'n** mgms/50g.	Conductivity of Water-Gypsum Sol'n mmhos/cm.
14	0	-	26.7	-	-
	4	-	26.5	-	-
	5	+	27.8	1.1	1.1
15	0	-	169.8	-	4.5
	8	-	183.2	13.4	5.1
	12	+	190.0	20.2	5.3
16	0	-	45.8	-	0.9
	10	-	81.3	35.5	1.8
	12	+	86.4	40.6	2.0
17	0	-	42.0	-	0.9
	8	-	73.3	31.3	1.5
	10	+	78.8	36.8	1.7
18	0	+	651.0	-	15.0
	2	+	-	-	-
	4	+	703.0	52.0	15.0
19	0	-	61.0	-	1.2
	12	-	112.0	51.0	2.1
	14	+	120.0	59.0	2.3
20	0	+	175.0	-	5.6
	2	+	180.0	5.0	5.8
21	0	-	45.0	-	0.9
	10	-	78.0	33.0	1.7
	12	+	85.0	40.0	1.9
22	0	-	102.0	-	1.7
	45	-	153.0	53.0	2.8
	55	+	155.0	55.0	3.1
23	0	-	81.0	-	1.4
	10	-	116.0	35.0	2.1
	12	+	124.0	43.0	2.3
24	0	-	12.2	-	0.3
	4	-	18.8	6.6	0.7
	6	+	20.6	8.4	0.8
25	0	-	13.9	-	0.4
	2	-	15.9	2.0	0.6
	4	+	16.0	2.1	0.8

* Expressed as tons per 4,000,000 lbs. soil

** Calculated from difference between sodium in the water extracts and in the gypsum solution extracts

Table 3. Exchangeable sodium before and after treatment with gypsum solution according to McGeorge-Breazeale and Schoonover methods for gypsum requirement and gypsum requirement of 25 soils determined by six methods.

Soil No.	Exchangeable Sodium: Before Gypsum Treatment		Exchangeable Sodium: After McGeorge-Breazeale Treatment	Exchangeable Sodium: After Schoonover Treatment	Gypsum Requirement As Determined By Methods Of: McGeorge-Breazeale	Schoonover	Shawarbi Abdel-Bar	Van Beekom	Cottenie	U. S. Salinity Laboratory
	m.e./100g.	%	%	%	T/A	T/A	T/A	T/A	T/A	T/A
1	1.4	6.5	0.5	0.9	5	4	3	1	1	2.4
2	4.4	14.9	1.0	2.0	8	9	8	9	6	7.5
3	6.4	18.8	2.9	2.1	10	12	10	14	10	10.9
4	0.6	10.9	1.8	3.6	4	1	4	0	1	1.0
5	1.5	6.8	0.9	2.3	6	4	4	1	2	2.6
6	9.5	56.7	23.4	29.4	6	10	10	23	16	16.2
7	9.1	49.4	22.9	22.8	15	17	15	22	16	15.5
8	6.7	31.7	6.2	5.2	15	17	14	15	11	11.4
9	0.2	1.7	1.8	2.6	2	5	2	0	0	0.3
10	0.7	5.2	1.5	2.9	2	6	2	0	1	1.2
11	3.3	12.1	2.2	2.6	5	6	4	6	5	5.6
12	2.7	15.8	3.5	8.8	6	6	6	5	4	4.6
13	2.0	12.5	1.9	3.1	0	5	5	3	3	3.4
14	1.2	6.8	1.1	2.8	5	4	4	1	1	2.0
15	4.5	35.0	9.4	13.3	12	16	11	9	-	7.7
16	7.4	18.5	4.5	3.0	12	14	4	17	11	12.6
17	7.2	23.4	6.2	5.2	10	15	8	17	12	12.3
18	7.4	44.3	19.7	13.2	4	8	1	17	13	12.6
19	8.9	49.5	10.6	9.5	14	17	12	21	15	15.2
20	1.2	5.6	3.7	5.6	0	-	-	1	2	2.0
21	7.2	23.6	5.9	5.2	12	13	7	17	13	12.3
22	35.2	82.3	37.0	30.2	55	54	40	93	61	59.8
23	5.2	41.5	28.8	38.4	12	11	13	12	9	8.9
24	1.6	5.5	3.4	1.7	6	4	3	2	2	2.7
25	1.1	8.8	3.2	5.6	4	2	3	1	2	1.9

The principal difference between the Schoonover and McGeorge-Breazeale methods is the ratio of weight of soil to volume of gypsum solution and the method used to determine the end point which represents the gypsum requirement of the soil. Both methods employ a technique in which a definite weight of soil is shaken with a solution of known gypsum content.

In columns 4 and 5 of Table 3, the residual percentage exchangeable sodium, as m.e./100 g. in the exchange complex is shown for the two methods. These values represent the exchangeable sodium in the soil not replaced by calcium during the test. The residual exchangeable sodium in the soil after these tests on the basis of a comparison of individual soils, shows some variation. These differences only occur in an occassional soil sample.

A similar and somewhat irregular variation is evident in the gypsum requirement values. In 15 out of 24 soils, the gypsum requirement values, as obtained by the Schoonover method, are higher than those obtained by the McGeorge-Breazeale method, but the differences are not great. These data indicate that the Schoonover method may give slightly higher gypsum requirement values.

It is significant that, despite a material reduction in exchangeable sodium during the test, both methods show that a satisfactory exchange of Ca for Na was not obtained for the soils with high exchangeable sodium content.

A comparison of the two methods is given in Figure 1 and 2, in which m.e. exchangeable sodium is plotted against tons gypsum per acre-foot of soil as determined by the two gypsum requirement methods. These charts show a very good correlation except for a few of the soils. For these exceptions, the variations from the mean are explained by the soil analysis data in Table 1. For soils 6 and 18, gypsum requirement values fall below the mean in both methods, and lower by the McGeorge-Breazeale method than by the Schoonover method. These soils are highly saline types, and additional gypsum requirement tests were made on them after partial desalinization in the laboratory. Soil 7 is the same as 6 after partial desalinization and soil 18 after partial desalinization is 19. It will be noted that both these soils after desalinization fall close to the line which represents the mean. This illustrates how sodium salts interrupt the replacement of Na by Ca and shows that highly saline soils should be partially desalinized before testing for gypsum requirement. It is of interest that the interference from salinity was less in the Schoonover method.

On the "high" side of the mean, three soil tests appear to be in error. These are samples 8 and 15 for both methods, and 23 in addition by the McGeorge-Breazeale method. All three of these soils are "bad" black alkali types, which indicates that high gypsum requirement values will be obtained when the test is applied to this type. This high value probably is due to precipitation of a part of the calcium from gypsum as carbonate.

This study of the two methods indicates that the Schoonover and McGeorge-Breazeale methods yield slightly higher gypsum requirement values than is represented by the quantity of gypsum that would be required to replace all the Na if the efficiency of the exchange reaction were completely one of equivalent proportions between replaceable Na and soluble Ca in the gypsum solution. This is more or less expected in some alkali soils and particularly under field conditions because of a number of factors too detailed to discuss here.

Table 4. The sodium, calcium chloride, and sulfate content of a selected number of extreme soil types.

Soil Number*	Calcium (Ca)	Sodium (Na)	Chlorine (Cl)	Sulfate (SO_4)	Na to Ca Ratio
	ppm	ppm	ppm	ppm	
6	200	3916	10,800	3600	19.6
15	300	2160	480	5200	7.2
18	404	5920	19,040	1000	14.7
19	160	1160	1,600	200	7.3
20	2020	8560	8,560	1601	.9
22	100	1730	1,730	1400	17.0

*Number represent the same soils as given in Table 1.

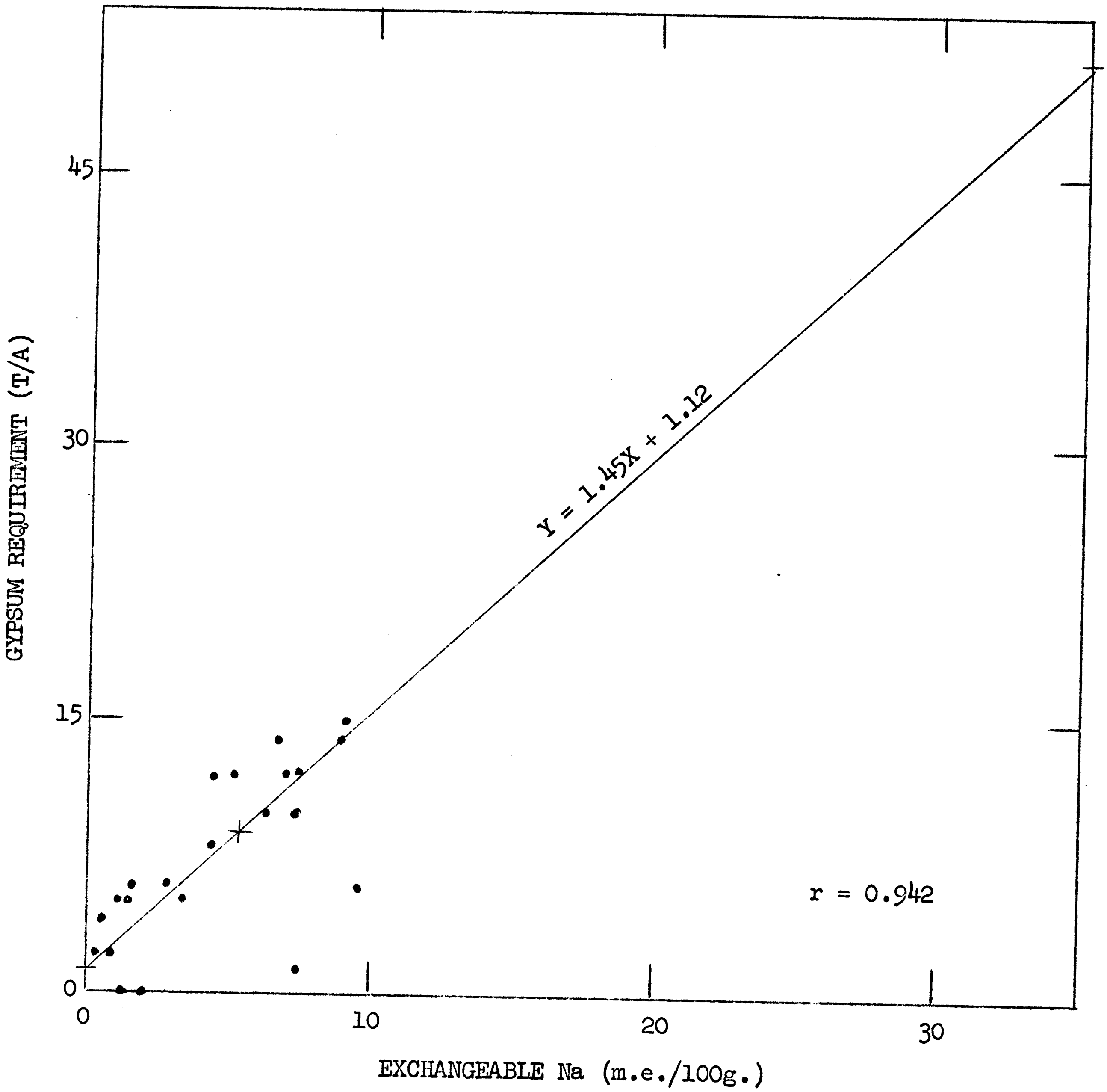

Figure 1. Regression line, m.e. Na per 100 grams soil and gypsum requirement, McGeorge-Breazeale method.

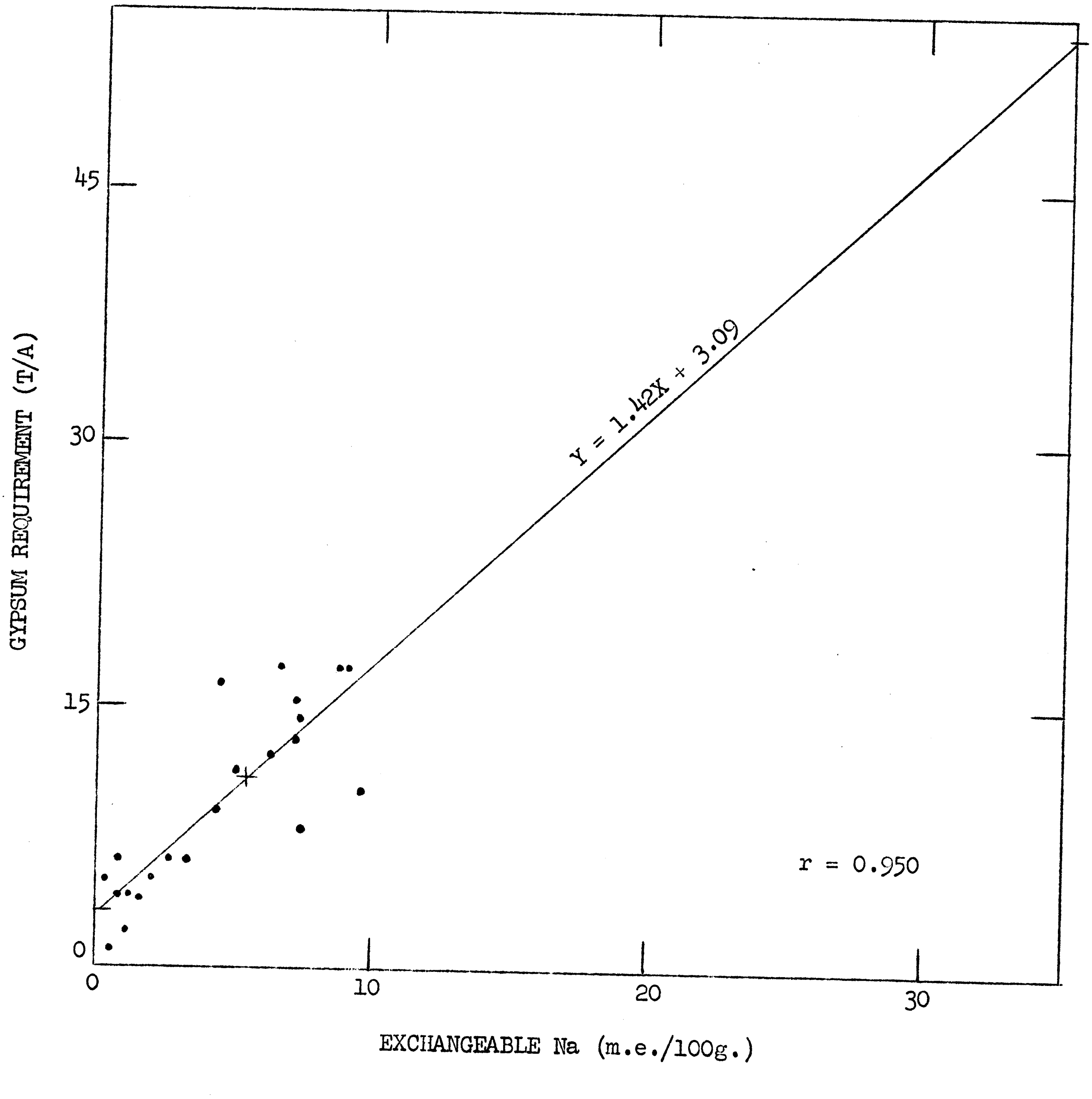

Figure 2. Regression line, m.c. Na per 100 grams soil and gypsum requirement, Schoonover method.

In most of the soils where the gypsum requirement values are appreciably lower than the calculated values, the soils are highly saline. Soil 6 is a saline-alkali soil from an area near Buckeye and soil 18 is from a saline area in the Roll Valley, Table 4. Both these soils gave low gypsum requirement values, that is, below the mean. The data in Table 4 indicate that the Na to Ca ratio is very high in these soils. In order to confirm the assumption that the gypsum requirement values were too low, 500-gram portions of these soils were treated in the laboratory with quantities of gypsum equal to the quantity arrived at by the McGeorge-Breazeale gypsum requirement method. These treated soils were then washed with water on a Buchner funnel to get the full effect of the gypsum, dried, and ground to pass a 20-mesh sieve. Capillary rise and infiltration rate tests were made on these soils. There was no response in either soil to the quantity of gypsum applied if the capillary rise test as reported in Figure 3 can be assumed to be suitable for determining water movement in the soil. The greater capillary rise in the untreated soil is a salinity effect. This is confirmed by the fact that capillary rise was reduced by partial desalinization of these two soils as represented by soils 7 and 19, in Figure 3.

Soil 15 is another soil that showed a high exchangeable sodium content after the treatment with gypsum solution in the gypsum requirement test. In this soil the salts are predominately sulfates, Table 4. Previous tests on the soil have shown appreciable amounts of sodium carbonate. In the gypsum requirement test for this soil, the precipitation of soluble calcium as calcium carbonate caused a high gypsum requirement value. Soil 20 is from a field to which an application of gypsum had been made. The acetone test on the saturation extract gave a positive test for gypsum and, therefore, a zero gypsum requirement.

Soil sample 22 is the most extreme black alkali type in this group of soils and has 35.2 m.e./100 g. exchangeable sodium and an exchangeable sodium percentage of 82.3. The analysis of this soil shows a very high sodium to calcium ratio and an excess of sulfates over chlorides. It is interesting to note that, despite the fact the exchangeable sodium after treatment with gypsum was very high, the capillary rise test shows a marked improvement in water movement in the soil. The same is also true for soil 23. The reason for the difference in response to gypsum treatment, despite the high residual exchange sodium after the gypsum test, as compared to soils 6 and 18, is not evident.

Soil 10 in Figure 3 is a sample from the University Experiment Farm at Mesa. This soil is not gypsiferous, shows a small gypsum absorption in the gypsum requirement test, and, in previous tests with gypsum, has shown little or no measurable response to gypsum treatment. The gypsum requirement test on this soil was 2 tons/acre and this indicates that soils which contain less than 1 m.e./100 g. soil of exchangeable sodium per 100 grams may be accepted as having a zero gypsum requirement. Van Beekom makes this assumption in interpreting the gypsum requirement test for Netherlands soils.

Soil 12 is a Cajon silt loam near Gilbert. The data in Table 3 show a near-complete replacement of Na during the gypsum requirement test. The graph for the control soil and the gypsum-treated soil shows that the gypsum treatment in this case was effective in improving water movement as capillary rise.

Soils 13 and 14 are from the Yuma Valley where Colorado River water has been used for many years. Soil 14 is the same as soil 13 except that it was partially desalinized in the laboratory. The McGeorge-Breazeale method showed a zero gypsum requirement for soil 13 because the water extract gave a positive test for gypsum. After partial desalinization and removal of the soluble gypsum,

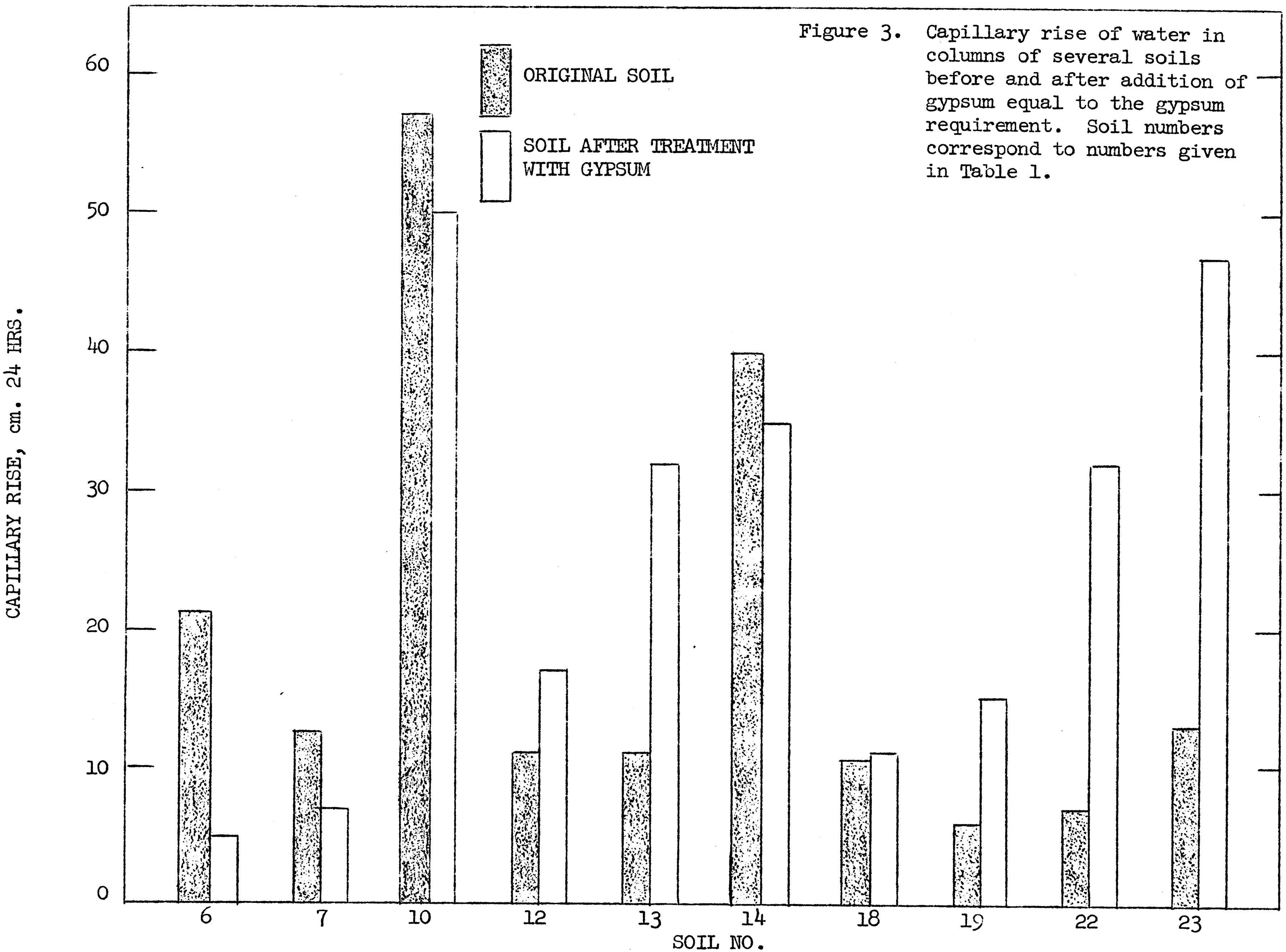

Figure 3. Capillary rise of water in columns of several soils before and after addition of gypsum equal to the gypsum requirement. Soil numbers correspond to numbers given in Table 1.

the soil showed a gypsum requirement of 5 tons per acre, which is in close agreement with the Schoonover values for both soils. It will be noted that the capillary rise tests in Figure 3 show a response to gypsum in soil 13, but not in soil 14. The results obtained here illustrate the value of leaching, which, in this particular case, was not possible in the field because of a high water table. Even though the soil was slightly gypsiferous, the high Na to Ca ratio in the soil solution interfered with replacement until the soil was desalinized. The capillary rise for this soil shows improvement in water movement from gypsum when the salts are present, but no improvement from gypsum after desalinization.

Shawarbi and Abdel-Bar Method - An ingenious method for determining the gypsum requirement of a soil is that of Shawarbi and Abdel-Bar (9) in which they recommend that 10 gram of soil in a water suspension be titrated with 0.02 normal sulfuric acid until the pH of the soil suspension reaches 8.0 to 8.3. The number of milliliters of 0.02 normal sulfuric acid required represents the tons of gypsum/acre- 20 cm. to "effect the desired reclamation." The gypsum requirement values obtained by this method are given in Table 3. The conversion from milliliters 0.02 normal sulfuric acid to tons gypsum/acre by this method is on the basis of an acre 20 cm. depth of soil (about 8.25 inches) and not/acre foot depth. This explains the lower gypsum requirement values. This method is rapid and simple. The principal requirements in the way of apparatus are a stirring device and a pH meter. It was our experience that the titration proceeds satisfactorily to about pH 8.5. Below this pH value in the soil suspension it is difficult to detect a stable end-point in highly calcareous soils. This may explain some of the irregularities in the values obtained with this method. Perhaps a more accurate end-point may be obtained with practice and a study of the conditions that influence the stability of the end point because Shawarbi and Abdel-Bar used soils containing 10 to 12 percent calcium carbonate when developing their method.

The apparent errors, that is the variations from the mean are similar to those obtained in the Schoonover and McGeorge-Breazeale methods. The gypsum requirement values obtained for the black alkali soils are higher than the mean and the values for the highly saline soils are lower than the mean. These three methods have an apparent advantage over the methods which require a determination of exchangeable sodium and exchange capacity in that the latter do not measure the gypsum used in the reaction with sodium carbonate.

U. S. Regional Salinity Laboratory Method - This method for determining the gypsum requirement of the soil (10) is based on the replaceable sodium content and the exchange capacity of the soil. Its application is illustrated as follows: "Suppose the 0 to 12-inch layer of alkali soil contains 4 m.e. of exchangeable sodium/100 g. and a cation exchange capacity of 10 m.e./100 g. The exchangeable sodium percentage is 40. It is desired to reduce the exchangeable sodium percentage to 10. This will necessitate the replacement of 3 m.e. of exchangeable sodium/100 g. Assuming quantitative replacement, it will be necessary to apply the amendment at the rate of 3 m.e./100 g. of soil." By referring to a table given in the reference 'which relates tons gypsum and sulfur/acre-foot of soil to m.e. of sodium/100 g. of soil, it is found that 5.2 tons of gypsum or 0.96 tons of sulfur are required." In their calculations, 1.7 tons gypsum/acre-foot of soil are required for the replacement of 1 m.e. exchangeable sodium/100 g. of soil. By this method, gypsum applications can be made on a basis equivalent to the total replaceable sodium present in the soil or for reduction in exchangeable sodium to any other sodium percentage. In the data given in Table 3, the gypsum requirements given are calculated on the basis of the total exchangeable sodium in the soils.

For the convenience of the reader, the equivalents for several soil correctives, as taken from the above reference, are given as follows:

	Tons equivalent to 1 ton sulfur
Sulfur	1.00
Lime sulfur (polysulfide)	4.17
Sulfuric acid	3.06
Gypsum	5.38
Iron sulfate	8.69
Aluminum sulfate	6.94

Netherlands Method - In 1953, the gale spring tides along the Netherlands coast were the most violent in many centuries and a large area of agricultural land was flooded by sea water. The soil became impregnated with soluble salt and adsorbed sodium. In developing a program of reclamation, a method was developed for determining the gypsum requirement of the soil. They were most concerned with restoring the structure of the soil and were, therefore, more interested in clay soils than in sandy soils. The Netherlands' method is based on the determination of the exchangeable Na in the soil and so is somewhat related to the method proposed by the U. S. Regional Salinity Laboratory. They recognize that it is not advisable to use gypsum on sandy soils in which the replaceable Na is less than 1 m.e./100 g.

The Netherlands' method developed by Van Beekom, et al. (11) is essentially a method developed from a series of gypsum tests in the field. From these tests, a chart was prepared by plotting m.e. Na/100 g. soil against tons gypsum/hectare which gave response in the field. From these results, an equation $a = 2.2(b-1)$ was developed in which a = amount of gypsum in tons per hectare needed for agriculturally-satisfying conditions; b = amount of exchangeable Na, just after draining in the upper 10 cm. of soil expressed as m.e./100 g. Therefore "b" is reduced by -1 on the basis that no gypsum is needed in soils containing less than 1 m.e. Na/100 g. - - "in such soils either no break-down of structure occurs or agriculture is not seriously affected by it."

If the problem is on very sandy soils, gypsum dressings are not recommended because, with proper water use, the excess Na will be removed by leaching or natural recovery. In the calculation, natural recovery must be taken into account and, therefore, the amounts of gypsum will be lower than might be expected from the initial Na content of the soil.

The data on gypsum requirement obtained from the Netherlands' method are given in Table 3 and Figure 5. For 15 of the 25 soils, the gypsum requirement value are higher than the Salinity Laboratory values. Moreover, they are higher than the values obtained by all other methods, particularly for the soils that are very high in exchangeable sodium. The high value for soil 22 is of particular interest as it is not out of line with the mean of the values obtained for other soils.

Cottenie Method - Belgium also was confronted with a reclamation problem because of inundation of land by sea water in 1953. Gypsum was extensively used in the reclamation program, and in the course of the reclamation, a gypsum requirement test was developed by Cottenie (2). This method is also based on the replaceable Na in the soil. The following factors are considered: (a) Ca to Na ratio, (b) the quantities of Na and Ca exchangeable by ammonium acetate, and (c) the soil type. The following are determined by the ammonium acetate method:

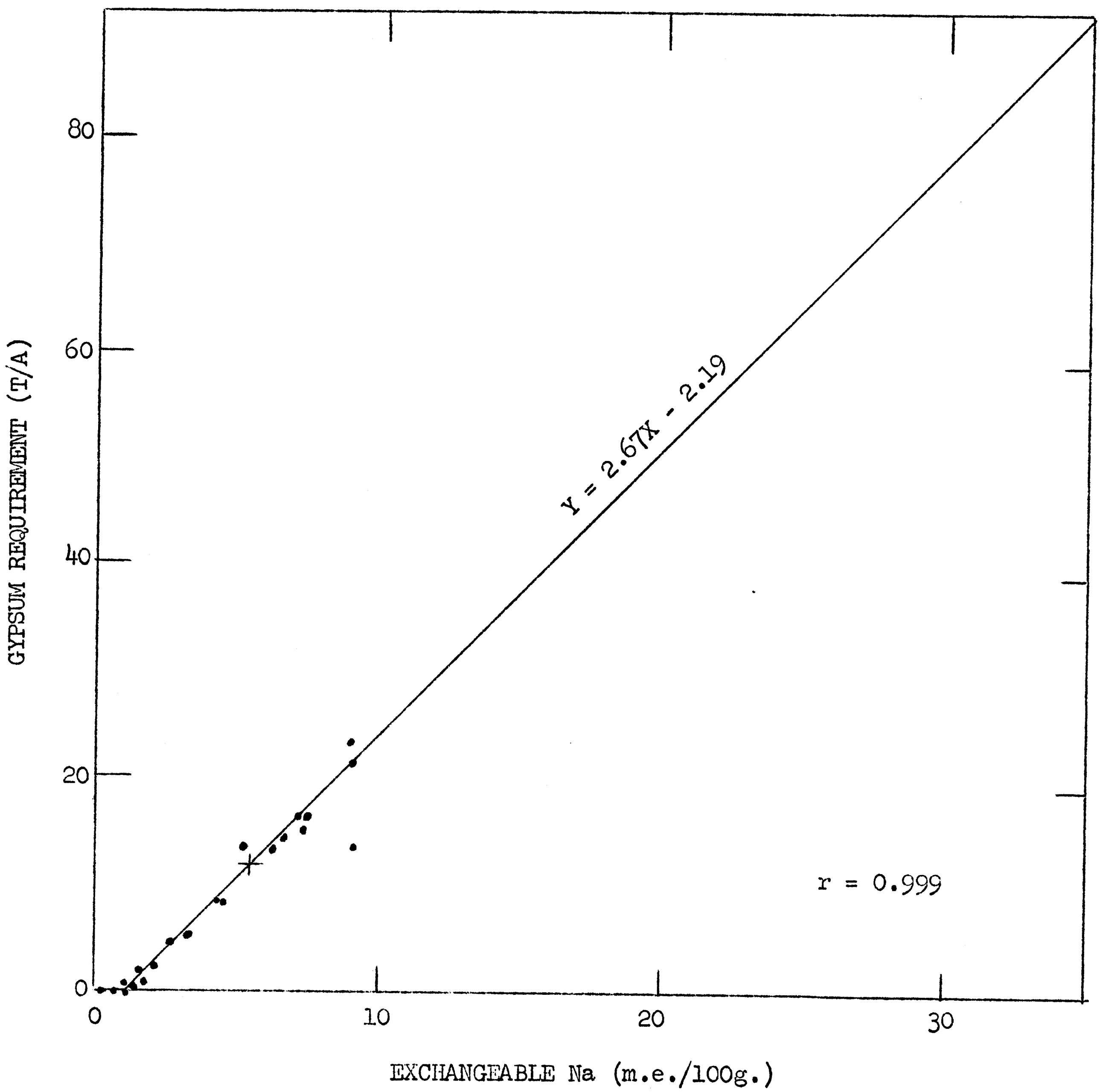

Figure 4. Regression line, m.e. Na per 100 grams soil and gypsum requirement, Shawarbi and Abdel-Bar method.

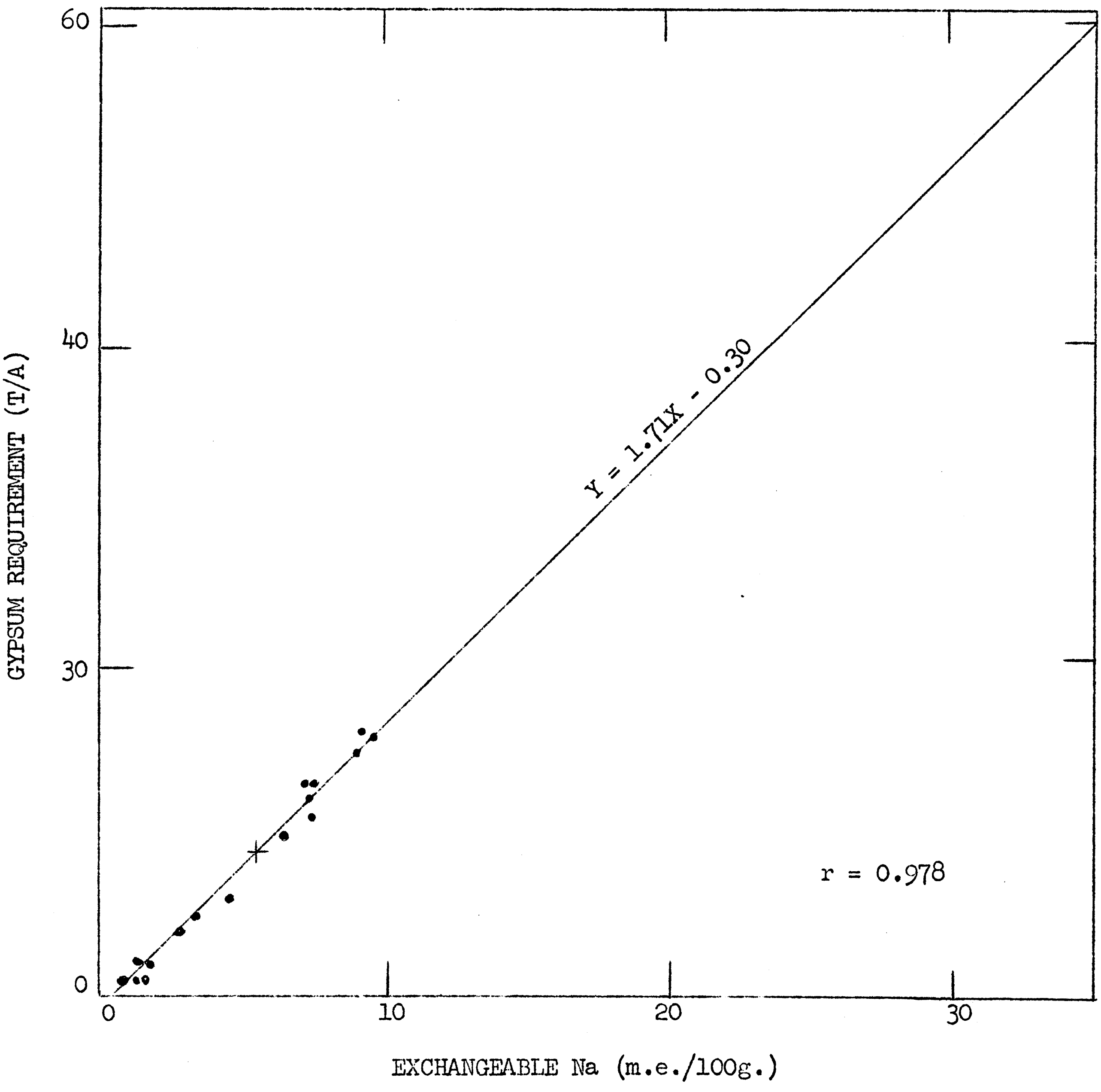

Figure 5. Regression line, m.e. Na per 100 grams soil and gypsum requirement, Netherlands method.

a. Number of m.e. Ca exchanged/100 g. of soil, or number of gram-equivalents Ca exchanged/100 kg. of soil.

b. Number of m.e. Na exchanged/100 g. of soil, or number of gram-equivalents Na exchanged/100 kg. of soil.

From these data the objective is to restore the ratio of Ca to Na to the value of 25. The calcium required for sodium replacement is represented by X in the equation $\frac{a + X}{b - X} = 25$. By doing this, "a" is increased to a + X, while as a result of repression, the existing quantity of Na becomes b-X. The value X is now determined from the equation given above which may be written $X = b - \frac{a}{25}$ g. equivalents gypsum/100 kg. of soil. On the basis that a greater amount of gypsum is needed for reclamation of heavy soils, a factor is used for taking this into account as follows:

Clay percentage less than 15	f = 1
Clay percentage between 15 and 30	f = 1.5
More than 30 percent clay	f = 2

No gypsum is recommended for soils in which the Ca to Na ratio is at least 25. The gypsum requirement values obtained with this method are given in Table 3 and Figure 6. There is a remarkable agreement between the values obtained by this method and the calculated values obtained by multiplying m.e. exchangeable sodium by 1.7 as recommended by the U. S. Regional Salinity Laboratory.

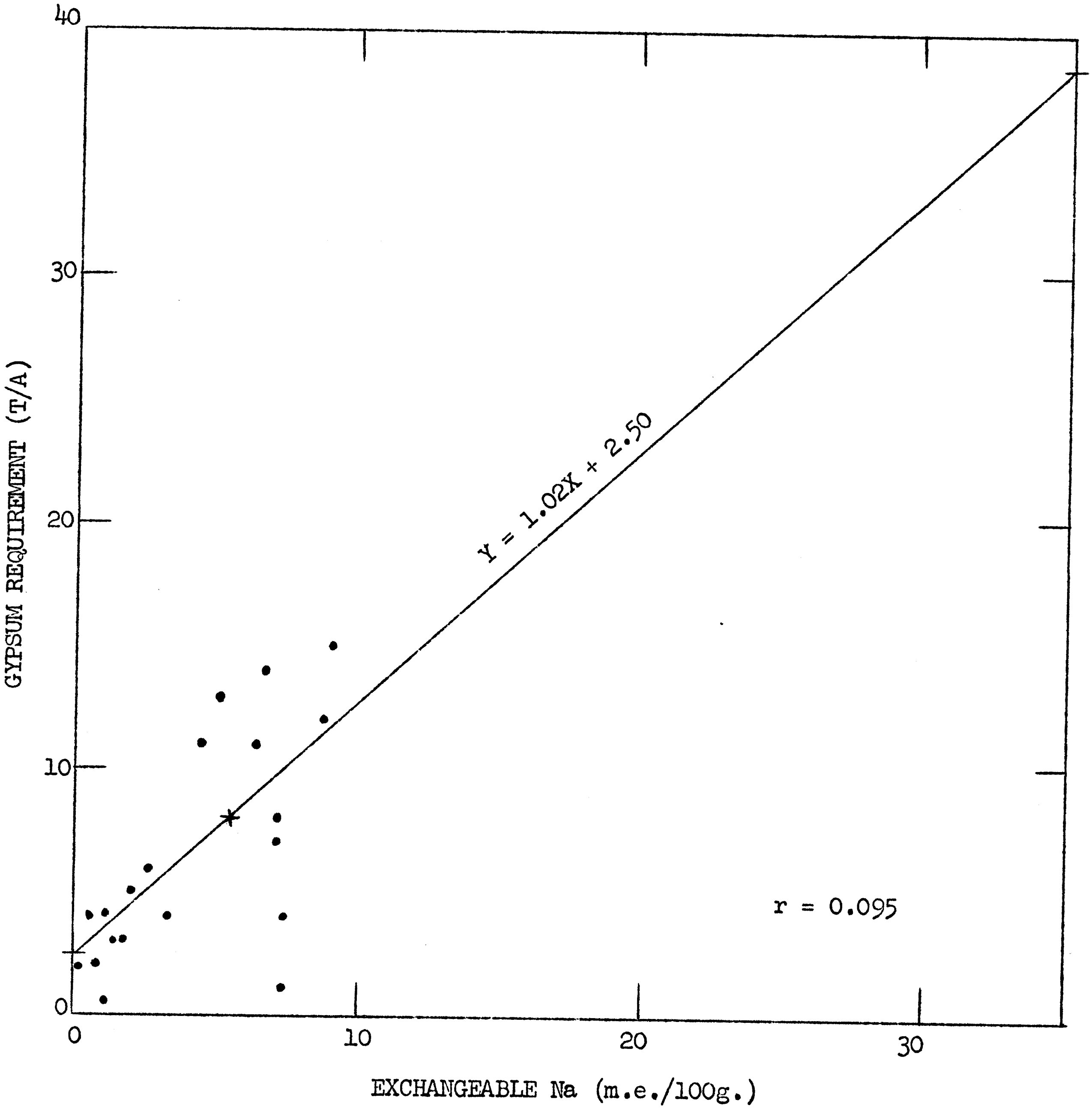

Figure 6. Regression line, m.e. Na per 100 grams soil and gypsum requirement, Cottenie method.

DISCUSSION OF RESULTS

In view of the close linear relation between exchangeable sodium and tons gypsum/acre-foot of soil obtained by all the methods, the correlation coefficients "r" and linear regressions were calculated. The scales were then adjusted so as to have each set of data on the same-sized graph. The experimental points were plotted and the regression lines drawn according to appropriate formulae. By adjusting the scales to fit the data, the point for soil 22 always was exactly in the upper right hand corner. This is significant because of the very high sodium percentage in this soil. The cross on the regression line is the mean for all data in the graph. The correlation coefficients and the regression equations for the five gypsum requirement methods shown in Figures 1, 2, 4, 5, and 6 are as follows:

1.	McGeorge-Breazeale	$r = 0.942$	$Y = 1.45 + 1.12$
2.	Schoonover	$r = 0.950$	$Y = 1.42 + 3.09$
3.	Netherlands	$r = 0.999$	$Y = 2.67 - 2.19$
4.	Cottenie	$r = 0.978$	$Y = 1.71 - 0.30$
5.	Shawarbi	$r = 0.905$	$Y = 1.02 + 2.50$

These data show that for each method, the gypsum requirement values are very significantly correlated with m.e. exchangeable sodium/100 g. of soil. There is, however, a difference between regression equations for the different gypsum requirement methods and the location of the regression lines with respect to each other in the several charts.

The highly significant correlations between gypsum requirement values and exchangeable sodium for each of the methods suggest that a factor could be used to calculate the gypsum requirements for all methods to a common gypsum requirement value or to calculate one from another.

There is a good agreement between the Schoonover and McGeorge-Breazeale methods despite the great difference between the weight of soil and volume of gypsum solution used in the two methods. Both methods indicate that the values obtained are more accurate on the soil after desalinization than when the salines are present. The data emphasizes the need for desalinization in the field in order to accomplish a maximum percentage of sodium replacement; however, there are other factors in reclamation under field conditions which must be considered. Particularly, one must recognize that, accompanying desalinization in the field, there is a reduction in water penetration rate commonly known as a "freezing up". Since water penetration is so closely linked with effective reclamation, it appears advisable to add at least a part of the required gypsum before the first leaching in order to forestall "freezing up". This is particularly important for clay soils, but much less important for light-textured soils. In calcareous soils, one can always count on a certain amount of natural reclamation, in which soil calcium plays a part, once movement of water is started through the soil.

One significant observation in the course of this study was the high sodium percentage remaining in some of the soils after treatment with gypsum solutions in the gypsum requirement test, that is, replacement was far from complete. This excess of residual replaceable sodium in the exchange complex appeared to be a characteristic of the soils containing enough exchangeable sodium to be classified as black alkali soils. It has been the opinion of the writer, based on experience, that when sodium adsorption had been allowed to progress slowly in the field to the point where the exchangeable sodium percentage is that of a black alkali soil, and particularly when the high sodium percentage has existed for a prolonged period, the soil colloids undergo certain changes which are not easily corrected by application of gypsum. The results obtained with the soils of high sodium percentage in this study, that is, incomplete replacement of sodium, may offer an explanation of this. The question arises as to whether a part of the exchangeable sodium is more firmly bound by prolonged dominance of a high percentage of sodium in the clay minerals, or, is it locked up in the exchange complex during the initial and rapid replacement that follows the contact of the clay minerals with the gypsum solution? We do know that gypsum treatments are far more effective in alkali reclamation when the soil is allowed to dry thoroughly after the first or second leaching following the gypsum application.

The titration method of Shawarbi and Abdel-Bar appears to warrant further study. It has merit of speed which is essential in a quick method for alkali soil appraisal and the correlation between gypsum requirement by this method and exchangeable sodium is highly significant.

The other methods that were included in this study, that is, those requiring a determination of exchange capacity and exchangeable sodium, do not offer anything which is not supplied by the procedure suggested in the Salinity Laboratory method. The Van Beekom tests show a good correlation between replaceable sodium and gypsum requirement but in the values appear to be too high. The results obtained with the Cottenie method are in amazingly close agreement with the calculations made by multiplying the milliequivalents exchangeable sodium by the factor 1.7.

One important point that should be mentioned is that in the gypsum requirement methods that are based on a calculation from the exchangeable sodium the values do not stray far from the mean as is the case for the other methods when high salinity and alkalility are present in the soil. However, if an appreciable amount of sodium carbonate is present in the soil this form of sodium is not accounted for in the determination of exchangeable sodium.

CONCLUSIONS

1. Gypsum requirement methods, in which an alkali soil is shaken with a gypsum solution, will yield gypsum requirement values which are correlated with the exchangeable sodium in the soil.

2. In general, there is no significant difference between the gypsum requirement values obtained by the Schoonover and McGeorge-Breazeale methods.

3. Highly saline soils will yield values which are lower than the mean and this error can be corrected by partially desalinizing the soil before making the gypsum requirement test.

4. Strongly alkaline soils, soils with high pH values, in which sodium carbonate is present, will yield values slightly above the mean. This is not an error in the method as part of the gypsum which functioned in correcting the alkalinity of sodium has definitely been used in correcting the alkalinity of the soil as a whole.

5. The titration method of Shawarbi and Abdel-Bar gave highly significant correlations between gypsum requirement values and exchangeable sodium. It appears to be useful and well adapted to the appraisal of alkali soils.

6. The Cottenie and Netherlands methods for the determination of gypsum requirement of alkali soils, which are based on the exchange capacity and exchangeable sodium, are somewhat similar to the U. S. Regional Salinity Laboratory method and are not classed as quick methods.

7. The gypsum requirement tests, in which an alkali soil is shaken with a gypsum solution, are useful in the quantitative application of gypsum in the reclamation of alkali soils and are acceptable substitutes for the methods in which the soil is analysed for exchange capacity and exchangeable sodium.

REFERENCES

1. Bower, C. A., Moodie, C. D., Orth, P., and Gschwend, F. B., 1954 Correlation of sugar beet yields with chemical properties of a saline-alkali soil. Soil Science 77: 443-451.

2. Cottenie, A. H. 1953. Over een methode voor het bepalen van de gipsbehoefte van met zoutwater overstrommde gronden. Deel 18, No. 4, State Agricultural College, Belgium.

3. Gardner, R. 1945. Some soil properties related to the sodium salt problem in irrigated soils. U.S.D.A. Tech. Bul. 902.

4. Hilgard, E. W., and Loughridge, R. H. 1895. Annual Report, Agricultural Experiment Station, University of California. 1895-96.

5. McGeorge, W. T. and Breazeale, E. L. 1951. Absorption of gypsum by semi-arid soils, Arizona Agricultural Experiment Station Tech. Bul. 122.

6. Moodie, C. D., 1954. Progress report to Technical Committee. Western Soil Research Committee Dec. 1954 (mimeograph).

7. Ricardo, N. G., 1951. Treatment of salty soils. Anal. Assoc., Pernua Tech. Azucareros. 2: 15-20 (C.A. 48: 1615).

8. Schoonover, W. R. 1952. Examination of soils for alkali. Univ. of Calif. Ext. Service (mimeograph).

9. Shawarbi, M. Y. and Abdel-Bar, A. A., 1954. A new method for estimating the actual amount of calcium sulfate required for reclaiming black alkali soils rich in soluble salts. Jour. Ind. Soc. Soil Science, 2: 15-20 (C.A. 49 (1955): 546).

10. Staff, 1954. Diagnosis and improvement of saline and alkali soils. U.S.D.A. Agriculture Handbook No. 60.

11. Van Beekom, C. W. C., Van Den Berg, C., De Boer, Th. A., Van Der Molen, W. H., Verhoeven, B., Westerhof, J. J., and Zurr, A. J., 1953. Reclaiming land flooded with salt water. Netherlands Jour. Agric. Science. 1: 1-31.

ACKNOWLEDGMENTS

The author is indebted to C. O. Stanberry for calculation of "r" values, regression equations, and preparation of Figures 1, 2, 4, 5, and 6. Also to S. C. Vandecaveye, New Mexico A. & M. College for translation of the Cottenie method.